

Chemistry

Lecture 13

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Liquids and Solids

Outline:

- ✚ Liquid State
 - Properties of liquids
 - Intermolecular forces
 - Hydrogen bonding
 - Vapour pressure
 - Boiling point and external pressure
- ✚ Solid State
 - Introduction
 - Types of solids
 - Ionic solids
 - Molecular solids
 - Crystal lattice and lattice energy

Liquid State

Properties of Liquids

📖 Spaces between them

- Molecules are fairly close to each other. There is very little space between them. As a result number of collisions is moderate. Therefore average K.E is also moderate

📖 Intermolecular forces

- They have stronger intermolecular forces than gases and the physical properties depend on the strength of these forces.

📖 Motion of Molecules

- Move with lesser speed due to larger forces of attraction among them. As a result they have lesser kinetic energy. However kinetic energy increases with temperature.

📖 Diffusion

- They show this phenomenon due to the movement of molecules but less than gases. The diffusion is slow due to less collisions between closely spaced liquids molecules i.e. drop of ink when added in water diffuses slowly due to relatively small empty spaces between the molecules.

📖 Compression (effect of pressure)

- A liquid cannot be compressed significantly by increasing the pressure as molecules are already in close contact with one another i.e. increases in pressure from 1 atm to 2 atm

reduces the volume of water to 0.0045 % which is negligible. However same pressure reduces the volume of a gas upto 50 %.

Expansion (effect of temperature)

- Liquids expand on heating because the intermolecular forces between them decrease. Increase of temperature increases the effective collisions between molecules. If the temperature is decreased, contraction of volume takes place which is useful in making thermometers i.e. mercury thermometer. If temperature rises, the mercury expands in the capillary tube.

Kinetic energy based on Kinetic Molecular Theory

- According to KMT, molecules due to strong intermolecular attractions have minimum movements and minimum collisions i.e. water molecules are closer to each other and have strong forces of attractions due to hydrogen bonding so have low K.E.

Intermolecular Forces	Intramolecular Forces
Present between molecules	Present within the molecule
Weaker forces	Stronger forces
Physical properties depends upon intermolecular forces	Chemical properties depends upon Intramolecular forces
Determines state of substance	Determines nature of substance
Dipole-dipole, dipole-induced dipole etc	Covalent bond, coordinate covalent bond

Dipole-dipole Forces;

- Positive end of one polar molecule attracts negative end of other polar molecule
- Present in polar molecules (HCl, CHCl₃)
- 1% as effective as a covalent bond
- Alkyl halides, aldehydes/ketones possess these forces
- Determines thermodynamic properties
- Depends on
 - Electronegativity difference \propto dipole dipole forces
 - 1/Intermolecular distance \propto dipole dipole forces

Dipole-induced dipole Forces;

- Present between polar and non polar molecules
- Also called Debye forces
- Positive end of polar molecule polarizes the electronic cloud of non-polar molecule inducing poles in it
- HCl + Ar, CO₂ in water, O₂ in water

London Dispersion Forces;

- Present between all type of molecules but not prominent in polar
- Non polar molecules have only these forces
- Temporary forces present between instantaneous dipole of one molecule and induced dipole of other molecule
- Factors:

Size of Electronic Cloud

- ✓ Greater the size of atom/molecule/electronic cloud, greater will be the dispersion of electronic cloud
- ✓ This increases polarizability (measure of extent of dispersion), hence increases strength of these forces
- ✓ Boiling points in noble gases increases down the group
- ✓ Boiling points in halogens increases down the group i.e. F_2 [$-188.1^\circ C$ a gas] and I_2 [$+184.4^\circ C$ a solid]

Number of Atoms

- ✓ Greater the number of atoms, greater the dispersion and strength of forces increases
- ✓ In hydrocarbons boiling points increase with increases in number of atoms (molecular mass) and their physical states also change i.e. ethane [$-88.6^\circ C$ a gas] and hexane [$+68.7^\circ C$ a liquid]

Hydrogen Bonding

- ☞ Electrostatic force of attraction between a highly electronegative atom and partial positively charged hydrogen atom
- ☞ Condition for H-bonding is presence of (i) Partial positive H-atom (ii) E.N atom (F, N, O, rarely Cl)
- ☞ No. of H-bonds per molecule depends on (i) H attached to E.N atom (ii) Lone pairs on E.N atom
- ☞ H_2O (2 H-bonds per molecule); partial positive charged H-atoms develop strong interaction with highly E.N atom oxygen of other molecule
- ☞ HF and NH_3 (1 H-bond per molecule); HF forms zigzag structure (with bond angle 120°) where partially positive charged H-atom is entrapped between highly E.N F-atoms, due to strong H-bonding HF becomes the weak acid amongst all halogen acids [$HI > HBr > HCl > HF$]. In ammonia H-atom of one molecule develops H-bonding with N-atom of other molecule.
- ☞ Therefore, B.Pt's $\rightarrow H_2O > HF > NH_3$
- ☞ The strength of hydrogen bond is generally twenty times less than that of a covalent bond
- ☞ **Thermodynamic Properties**
 - Boiling points increases down the group in IVA hydrides due to increase in size ($CH_4 < SiH_4 < GeH_4 < SnH_4$)
 - H_2O , HF and NH_3 have higher boiling points in their respective groups due to strong H-bonding between their molecules.
 - Due to this water is in liquid state at room conditions while other members are gases ($H_2O > H_2Te > H_2Se > H_2S$)
 - Similarly HF is only in liquid state from group VIIA hydrides ($HF > HI > HBr > HCl$)
 - VA hydrides are gases ($SbH_3 > NH_3 > AsH_3 > PH_3$)
- ☞ Solubility of lower alcohol and lower carboxylic acids in water is due to H-bonding which they develop with water molecules
- ☞ Cleansing action of soaps and detergents is due to H-bonding
- ☞ Protein (helix forms due H-bonding between O of $C=O$ group and H of $-NH$ group), DNA (double helix of diameter 18-20 Å formed due to H-bonding between A and T (2 H-bonds), G and C (3 H-bonds))

- ☞ H-bonding is in food material (glucose, fructose, sucrose), paints, dyes, textile material have adhesive properties due to H-bonding

Structure of Ice:

- ☞ Water has tetrahedral structure with 2 corners occupied by lone pairs and 2 by H-atoms
- ☞ As temperature decreases,
 - ✓ Regularity increases
 - ✓ Volume increases (9%)
 - ✓ Empty spaces increases
 - ✓ Density increases up to 4°C and then after 4°C starts decreasing
- ☞ Maximum density of water is at 4°C
- ☞ Each O-atom in ice is surrounded by 4 H-atoms, 2 through covalent bond and 2 through H-bond
- ☞ Each H-atom in ice is surrounded by 2 O-atoms, 1 through covalent bond and 1 through H-bond
- ☞ Each molecule of ice has a structure just like diamond (tetrahedral)
- ☞ Overall it forms hexagonal crystal
- ☞ Due to formation of layer of ice on surface which acts as insulator and floats due to less density, fish survive in ponds in cold winter

Evaporation

- ☞ Surface phenomenon
- ☞ Escape of high energy molecules from surface
- ☞ Spontaneous process (continuous process)
- ☞ Occurs in open vessel
- ☞ Cooling process (Endothermic)
- ☞ Decreases due to humidity in air
- ☞ **Dependence**
 - ⚙ Directly related to temperature
 - ⚙ Directly related to surface area
 - ⚙ Inversely related to intermolecular forces

Vapour Pressure

- ☞ Pressure exerted by the vapours of the liquid in equilibrium with the liquid at a given temperature
- ☞ Dynamic process (Evaporation \rightleftharpoons Condensation)
- ☞ Closed vessel required
- ☞ Measured by manometer (accurate method)

$$P = P_a + \Delta h$$

P = Vapour pressure of the liquid at one atm pressure.

P_a = Atmospheric pressure.

Δh = Difference in the heights of the mercury levels in the two limbs of the manometer, giving us the vapour pressure of liquid.

☞ Decreases during rain

☞ **Dependence**

- ⚙ Directly related to temperature
- ⚙ Inversely related to size
- ⚙ Inversely related to intermolecular forces
- ⚙ Increase in V.P for water from 4.579 torr

to 9.209 torr when temperature changes from 0°C to 10°C. But increase is from 527.8 to 760 torr when temperature changes from 90°C to 100°C. (this is due to difference in strength of intermolecular forces at different temperatures)

☞ Does not depend upon amount and surface area

Name of compound	Vapour pressure at 20 °C (torr)
Isopentane	580
Ethyl ether	442.2
Chloroform	170
CarbonTetrachloride	87
Ethanol	43.9
Mercury	0.012
Glycerol	0.00016

Boiling Point

☞ A temperature at which the vapour pressure of the liquid becomes equal to the external atmospheric pressure

☞ At boiling point kinetic energy of molecules is becomes maximum and extra heat is used to break intermolecular forces

☞ The amount of heat required to vaporize one mole of a liquid at its boiling point is called its molar heat of vaporization (ΔH_v)

☞ $\Delta H_v \propto$ strength of intermolecular forces

☞ The molar heat of vaporization of water is 40.6 kJmol⁻¹ (to break H-bonds(mainly) and van der Waals forces)

☞ **Dependence**

- ⚙ Directly related to external pressure
- ⚙ Directly related to intermolecular forces

☞ **Boiling point of water;**

- ✓ At 1489 torr → 120°C (Usually pressure cooker)
- ✓ At 760 torr → 100°C (Sea level)
- ✓ At 700 torr → 98°C (Murree)
- ✓ At 323 torr → 69°C (Mount Everest)
- ✓ At 23.7 torr → 25°C

☞ **Applications;**

- ✓ In pressure cooker, external pressure is increased to increase the boiling point and decrease the cooking time
- ✓ In vacuum distillation, external pressure is reduced to decrease the boiling point of sensitive liquids
- ✓ Advantages
 - Avoid the decomposition of sensitive liquids i.e. glycerin decompose at its boiling point of 290°C (at 1 atm) , so its boiling point is reduced to 210°C with external pressure of 50 torr
 - Decreases the time for the distillation process
 - Economical because less fuel is required

☞ Boiling point of diethyl ether is 34.6°C (due to weak London forces)

Liquid	B.P ($^{\circ}\text{C}$)	Liquids	B.P ($^{\circ}\text{C}$)
Acetic Acid	118.50	Carbontetrachloride	76.50
Acetone	56.00	Ethanol	78.26
Aniline	184.4	Naphthalene	218.00
Benzene	80.15	Phenol	181.80
Carbon disulphide	46.30	Water	100.00

Solids

- ◆ Solids are those substances which are rigid, hard, have definite shape and definite volume.
- ◆ The atoms, ions and molecules that make up a solid are closely packed.
- ◆ They are held together by strong cohesive forces.
- ◆ The constituent atoms, ions or molecules of solids cannot move at random.
- ◆ There exists a well ordered arrangement in solid
- ◆ **Simple cube;** (i) lattice points at corners (ii) coordination no. 6 (iii) 1 atom per unit cell
- ◆ **Face centered cube (FCC);** (i) lattice points at corners and centre of face (ii) coordination no. 12 (iii) 4 atoms per unit cell
- ◆ **Body centered cube (BCC);** (i) lattice points at corners and at centre of body (ii) coordination no. 8 (iii) 2 atoms per unit cell

Crystalline Solids (True solids)	Amorphous Solids (Pseudo solids)
Possess regular three dimensional arrangement of particles	No regular arrangement Also called Vitreous solids and Super cooled liquids
Sharp melting points	No sharp M.P (but melt over range of T)
Undergo clean cleavage	No clean cleavage
Definite geometry	Small regions of regularity called crystallites
They show the phenomenon of anisotropy (change in physical properties with changing the direction)	They show the phenomenon of isotropy (no change in physical properties with direction)
They have water of crystallization i.e. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	They do not have water of crystallization
Sugar, ice, diamond, Cu etc	Glass, plastic, rubber etc

Properties of Crystalline Solids

1. Geometrical Shape

All the crystalline solids have a definite, distinctive geometrical shape due to definite and orderly arrangement of atoms, ions or molecules in three dimensional space.

2. Sharp melting points

3. Undergo clean cleavage upon application of external pressure into small crystals of similar shape (as of original crystal) and size

- The breaking of large crystal into small ones is cleavage and the plane which contains the direction of cleavage is called cleavage plane.

- $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, NaNO_3 , $(\text{CH}_3\text{COO})_2\text{Ca}$ and Mica can easily be cleaved parallel to their surfaces

4. Anisotropy

Some of the crystals show variation in physical properties depending upon the direction. Such properties are called anisotropic properties and the phenomenon is referred to as anisotropy.”

The physical properties of crystalline solids like

- Refractive index
- Coefficient of thermal expansion
- Electrical and thermal conductivities

For example, electrical conductivity of graphite is greater in one direction than in another. Actually electrons in graphite are mobile for electrical conduction parallel to the layers only. Therefore, its conductivity in this direction is far better than perpendicular to the other direction.

5. Symmetry

- The repetition of faces, angles or edges when a crystal is rotated by 360° along its axis is called symmetry
- The process through which crystal was brought back to its identical position is called symmetry operation
- For example a regular cube is rotated about its axis at an angle of 90° , the 1st identical face is obtained. On rotating 180° , second identical face, and at 360° , four identical faces are obtained.
- An axis containing four identical faces is called four-fold axis of rotation
- Types: Center of symmetry, plane of symmetry, axis of symmetry, angle of symmetry

6. Habit of a Crystal

- The shape of a crystal in which it usually grows
- Crystals are usually obtained by cooling the saturated solution or by slow cooling of the liquid substance
- If the conditions are changed the shape of the crystal may change.
- For example, a cubic crystal of NaCl becomes needle like when 10% urea is present in its solution as an impurity.

7. Isomorphism

Isomorphism is the phenomenon in which two different substances exist in the same crystalline form. These different substances are called isomorphs of each other

- Independent of the chemical nature of the atoms and depends only on the number of atoms and their way of combinations
- Physical and chemical properties are quite different from each other
- ZnSO_4 and NiSO_4 orthorhombic (atomic ratio 1:1:4)
- Ag_2SO_4 and Na_2SO_4 are hexagonal (atomic ratio = 2:1:4)
- CaCO_3 and NaNO_3 are rhombohedral (atomic ratio = 1:1:3)

Isomorphs	Crystalline form	Atomic ratio
NaNO ₃ , KNO ₃	rhombohedral	1:1:3
K ₂ SO ₄ , K ₂ CrO ₄	orthorhombic	2:1:4
ZnSO ₄ , NiSO ₄	orthorhombic	1:1:4
NaF, MgO	cubic	1:1
Cu, Ag	cubic	1:1
Zn, Cd	hexagonal	1:1

- CO₃²⁻ and NO₃⁻ are triangular planar units (similar atomic ratio), while SO₄²⁻ and CrO₄²⁻ are both tetrahedral (similar atomic ratio).

8. Polymorphism

Polymorphism is a phenomenon in which a compound exists in more than one crystalline forms. That compound which exists in more than one crystalline form is called polymorphic, and these forms are called polymorphs of each other

- Same chemical properties, but they differ in the physical properties

Substance	crystalline forms
AgNO ₃	Rhombohedral, Orthorhombic
CaCO ₃	Trigonal and orthorhombic

HgI₂ (orthorhombic yellow form and tetragonal red form)

9. Allotropy

The existence of an element in more than one crystalline form is known as allotropy and these forms of the element are called allotropes or allotropic forms

- Same chemical properties, but they differ in the physical properties

Element	Crystalline forms
Sulphur, S	Rhombic, monoclinic
Carbon, C	cubic (diamond), hexagonal (graphite)
Tin, Sn	grey tin (cubic), white tin (tetragonal)

10. Transition Temperature

Temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. At this temperature, one crystalline form of a substance changes to another

- Always less than M.P

(i)	Grey Tin (cubic)	13.2°C	White Tin (tetragonal)
(ii)	Sulphur S ₈ (rhombic)	95.5°C	Sulphur S ₈ (monoclinic)
(iii)	KNO ₃ (orthorhombic)	128°C	KNO ₃ (rhombohedral)
(iv)	Na ₂ SO ₄ .10H ₂ O (hydrated)	32.38°C	Na ₂ SO ₄ (anhydrous) + 10H ₂ O
(v)	Na ₂ CO ₃ .10H ₂ O (higher hydrated)	32.02°C	Na ₂ CO ₃ .7H ₂ O (lower hydrated) + 3H ₂ O

Crystal lattice:

- Crystal lattice is an array of points representing atoms, ions or molecules of a crystal, arranged at different sites in three dimensional space
- These sites are called lattice sites or lattice points

Unit Cell:

- The smallest part of the crystal lattice has all the characteristic features of the entire crystal and is called a unit cell
- Unit cell on repetition in three dimensions forms the whole crystal
- Quantitative aspects of a crystal lattice are deduced from the size and shape of the unit cell
- There are three unit cell lengths a , b , c and three unit cell angles α , β and γ
- The angle ' α ' is between the lengths ' b ' and ' c ', the angle ' β ' is between the sides ' a ' and ' c ' and angle ' γ ' is between sides ' a ' and ' b '
- These six parameters of the unit cell are called unit cell dimensions or crystallographic elements

Ionic Solids	Molecular Solids
Constituents are ions	Constituents are molecules
Ionic bond b/w ions NaCl. KCl. KBr etc	Intermolecular forces b/w molecules i.e H-bonding/dipole or van der waals forces
Always solids at room temperature	Not always solids at room temperature
Hard, high M.P/B.P, low volatility	Soft, compressible, low M.P/B.P, high volatility, sometimes transparent to light
Closed structures due to non directional ionic interactions, so have high density	Can be polar (ice sugar) and non polar (iodine, sulphur , dry ice (solid CO ₂))
Do not exist as individual molecules	Exist as individual molecules
Formula mass term is used instead of molecular mass	Molecular mass term is used
Geometry will be same for different ionic solids if they have same cation and anion ratio i.e. NaCl and CsF have same	
Conductors only in molten or aqueous states	Bad conductors, low density than covalent and ionic solids
Highly brittle due parallel layers of ions	HCl, HF like solids like can be conductors in aqueous form
Soluble in polar solvents	Polar soluble in polar solvents and non polar in non polar solvents
Show isomorphism and polymorphism	
Very fast reactions	Polar have more M.P/B.P than non polar
Structure of NaCl	Structure of Iodine
Face centered cubic	Face centered cubic
Distance b/w similar ions is 5.63 °A	Grayish black di-atomic molecule
Distance b/w opposite ions is 2.815 °A	Show metallic luster
Coordination no. of Na ⁺ = 6, Cl ⁻ = 6	Sublime solid
Independent molecule of NaCl exist in only vapor phase never in solid	Bond length in different in vapor and solid phases
8 Cl ⁻ are at corners (each corner part of 8 unit cells)	Solid phase = 271.5 pm Vapor phase = 266.6 pm
1 Cl ⁻ per unit cell comes from all corners	Soluble in non-polar solvents
6 Cl ⁻ are at faces (each face part of 2 unit cells)	Soft with low M.P
3 Cl ⁻ per unit cell comes from all faces	

Total no. of Cl ⁻ per unit cell = 4	-----
Total no. of Na ⁺ per unit cell = 4	-----
Total no. of NaCl per unit cell = 4	-----

Lattice Energy

- Energy released when one mole of ionic compound/crystal is formed from its gaseous ions or
- Energy absorbed when 1 mole of ionic crystal is broken into its gaseous ions



- L.E \propto Charge/size (charge density)
- LiCl > NaCl > KCl > RbCl NaF > NaCl > NaBr > NaI

Factors that Affect the Shape of Ionic Solids

1. Electrostatic Force of Attractions

Ionic solids are composed of cations and anions which are held by strong ionic bond and have definite shape

Formation of NaCl is formed when Na⁺ ion (formed by loss of electron by Na) combine with Cl⁻ ion (formed by gain of electron by Cl), as result energy is released and cubic structure is obtained for NaCl

2. Radius Ratio

Shape of ionic solids depends on radius ratio of cations and anion

Body centered cubic $\frac{r_+}{r_-} = 0.732$ or above

Octahedral $\frac{r_+}{r_-} = 0.414$ to 0.732

Tetrahedral $\frac{r_+}{r_-} = 0.22$ to 0.414

Triangular $\frac{r_+}{r_-} = 0.15$ to 0.22

- NaCl = 0.522 Octahedral arrangement or Cubic structure
- CsCl = 0.93 Body centred cubic arrangement
- ZnS = 0.40 Tetrahedral arrangement

3. Poor Conductivity

Do not conduct electricity in solid state, so shape of crystal remains as such.

When solvent(water) is added to ionic solid i.e. NaCl, the crystal lattice is broken and ionic solid changes into cation and anion due to high dielectric constant of water. In this way the shape of crystal is ruptured.